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PREPARATION OF INORGANIC CATALYST BASED HEMATITE (α-Fe_2O_3) COMPOUND EXTRACTED FROM ACEH IRON ORE MINERAL AND ITS CATALYTIC ACTIVITY ON TRANSESTERIFICATION OF COCONUT OIL

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Abstract. Hematite (Fe_2O_3) was successfully extracted from the Aceh iron ore mineral by precipitation method with employing sulphuric acid (H_2SO_4) as chemical agent. Furthermore, the extracted hematite was modified with sodium metal (K), namely it doped with NaOH of 5% and 10% (w/w), respectively. Based on the characterization results using XRD and SEM- EDS proved that modified catalyst (Na_2O/Fe_2O_3) with their homogeneous size were resulted while the hematite (Fe_2O_3) particles was dopped with NaOH at its low concentration of (5% wt/wt), however while doping with the higher concentration of NaOH (10% w/w), agglomeration was taken place among the catalyst particles in which decreasing the surface area of the modified catalysts. Finally, the modified catalyst (Na_2O/Fe_2O_3) was successfully applied as an inorganic catalyst on transesterification of coconut oil and methanol (T = 55 – 60^{o}C, 2 h) for forming methyl esters as biodiesel compounds.

Keywords: modified catalyst, Fe_2O_3, hematite, sodium, biodiesel synthesis

I INTRODUCTION

Indonesia is one of tropical countries which has abundant mineral resources including iron mineral. The iron mineral is widerly found in Indonesia, particularly in Aceh Besar, North Aceh, and Sabang region, where as the total deposit of the mineral reserve is aproximately about 7.2 million tons. Unfortunelly, most of the local mineral has been used as cement aggregate only at PT. Semen Andalas Indonesia (SAI) located in Lhoknga, AcehBesar [2,6-7,10]. Connecting with its chemical aspect, there are several studies had been done in order to have more detail information about the chemical composition of the iron sand mineral, particularly related to percentage of iron mineral samples found at different location in Aceh, such as Lam Panah (Aceh Besar) and Mon Keulayu (Bireuen) and Lhoong Aceh Besar, [5,10], which was confirmed that hematite (α-Fe_2O_3) are the main compound contained in the iron ore mineral with 61.32 - 93,88 (% wt/wt). Considering its geometrical structure, hematite (α-Fe_2O_3) is one of iron oxides among magnetite (Fe_3O_4) and maghemit (γ-Fe_2O_3). Hematite compound (α-Fe_2O_3) become most popular of among the iron oxide compounds due to their polymorphic properties, biochemical uniqueness, magnetic, catalytic and other properties [6-7,9-12]. Hematite has a rhombohedral shape with a central hexagonal structure and a dense oxygen lattice. This causes hematite is believed to be a special choice for many important applications such as sensors, catalysts, data storage materials, fine ceramics, pigments, and photoelectrochemical cells [1]. Despite having abundant reserves in Aceh, there is no report for application of the hematite α-Fe_2O_3 as an inorganic catalyst on biodiesel synthesis. Therefore, concerning on the inexpensive and green application of hematite as an inorganic catalyst for biodiesel synthesis [1], we carried out this research work, namely preparing hematite (α-fe_2O_3)

from Lhong iron mineral in Aceh Besar and modified the extracted hematite with sodium metal for application as inorganic catalyst on biodiesel synthesis, so that it could be applied as an alternatif inorganic catalyst for biodiesel synthesis in future.

II. METHODOLOGY

The sample used in this research was iron ore mineral originating from Lhoong, Aceh Besar. The samples were separated from other oxide constituent (impurities) using bar magnet, so that increasing the purity of iron content. Furthermore, iron ore sand is mashed with metal mortar changed into smaller particle size. The particle size then was homogenized by sieving using a 100 metal mesh. The size of the produced solid particles is around 150 µm. Then, the iron sand powder was used as raw material for hematite preparation. The hematite was prepared from the Lhong iron ore mineral (powder) using precipitation method reacted with sulphuric acid (95% v/v of H_2SO_4) in a chemical vessel in the same manner as it reported in previous work [2,7,8]. Each chemical vessel was stirred evenly and left for seven days at room temperature to form a yellow-green spot throughout the sample.Each sample then was refined and calcined using a furnace at a temperature of 700^{o}C for 2 h [2,7,8].

Preparation of $Na_2O/\alpha\text{-}Fe_2O_3$ Catalyst

The synthesis of inorganic catalyst in this experiment was referred to the procedure which reported in previous study [1-5], where as in this experiment sodium hydroxide (NaOH) in various content (5% and 10% wt/wt) was impregnated on hematite ($\alpha\text{-}Fe_2O_3$) material, respectively. It was stirred and left at room temperature for ± 2 h. The heterogeneous mixture was dried at a temperature of 110^{o}C for ±2 h and followed by calcination process at an elevated temperature of up to 450^{o}C for 4 h for resulting in $Na_2O/\alpha\text{-}Fe_2O_3$ catalyst. The sythesized catalyst characterized using X ray diffraction (XRD) and Scanning Electron Microscope Energy Dispersive X-Ray Spectroscopy (SEM-EDS).

Catalytic Study on Transesterification Reaction of Coconut Oil.

At initial stage, in order to remove the water content, the raw coconut oil had been heated up to105^{o}C for 30 min. Then the coconut oil was left until reaching the room temperature (around 30^{o}C). The catalytic activity of the synthesized $Na_2O/\alpha\text{-}Fe_2O_3$ catalyst was carried out as it decribed in the following procedure. Hematite modified sodium catalyst ($Na_2O/\alpha\text{-}Fe_2O_3$) which its amount of 2.7g was mixed with 25 mL of methanol and put into in chemical vessel and stirred using a magnetic stirrer to activate for 15 min at a speed of 250 rpm, then the coconut oil was introduced into the mixture of catalyst and methanol. The heterogeneous mixture is heated at a temperature of 60^{o}C for 2 h. Upon completion this process, the liquid phase of the reaction product was transferred and left in a separating funnel so that consisting in two layers completely. The top layer of solution was removed and kept into a storage glass for its chemical analysis using Gas Chomatograpgy-Mass Spectrometry (GC-MS). This chemical analysis is intended to determine the chemical composition of the transesterification reaction.

III. RESULTS AND DISCUSSION

Figure 1(a) showed the iron mineral particles after mashing by means ofthe metal mortal, and separating using the metal mesh sieves producing fined iron sand powder with homogeneous particles in a size of around 150 µm. It can be seen that the iron sand particles become darker than its originalcolor. It could be assumed the physical process applied in this experiment, namely the mashing and the separation processes had enhanced the purity of iron oxides (FeO, Fe_2O_3 and Fe_3O_4) prepared from Lhong iron mineral.The extraction of hematite ($\alpha\text{-}Fe_2O_3$) was carried out by reacting the solid iron sand (powder) with H_2SO_4 solution.The chemical reaction produced the ferric sulfate compounds [$Fe_2(SO_4)_3$] in the reaction system,as it desribed in the following reaction:

$$Fe_2O_{3\,(S)} + 3H_2SO_{4\,(l)} \rightarrow Fe_2(SO_4)_{3(S)} + 3H_2O_{(l)}$$

It can be explained that the mashing process made on the iron mineral affected to increase the surface area of the material, so that leading to its optimum contact with H_2SO_4 solution during stirring process and produced suspension sample and finally, iron ion precipated as $Fe_2(SO_4)_{3(S)}$. This results indicates that the smaller particle size of iron oxides tends to cause the process of evaporation on material surface taken place more quickly. Furthermore, as showed in Fig. 1(b), after the two samples were left in the open air in which in the second day the greenish yellow color appears in several parts of the samples.Until the 7th day, the greenish yellow color covered almost all parts of the sample. The greenish yellow color indicated the formation of ferric sulfate [7], following calcination process at 700^{o}C for 2 h resulting in hematite with red color as shown in Fig.2(a). The red color indicated that hematite (α-Fe_2O_3) has been successfully prepared, as it illustrated in the following reaction:

$$Fe_2(SO_4)_{3(S)} + O_{2\,(l)} \rightarrow \alpha\text{-}Fe_2O_{3(S)} + SO_2^-{}_{(g)}$$

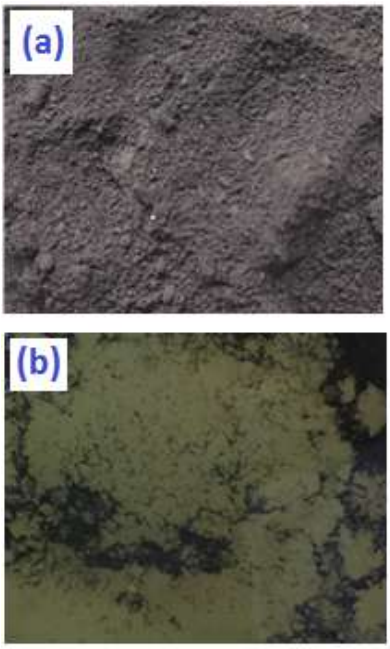

Figure 1; (a) fined iron sand particle in darkcolor after mashing and separation using the metal mesh (150 µm); (b).The formation of a greenish yellowcolor on iron mineral powder after treatment using H_2SO_4.

However, as it exhibited in Fig. 2(b), while the hematite doped with sodium, the color of the prepared material changed becoming darken red. It assumed that the same sodium ion has attached to the hematite surface changing its physical characteristics. In order to undertand the phases of metal oxides of the samples, XRD analysis has been carried outin this experiment. As it shown in Fig.3, it confirmed that the hematite compound has been succesfully prepared in this experiment, in which the XRD spectrum of the prepared compound obtained in this experiment is in very good agreement with a database of hematite compounds in the Inorganic Crystalography Open Data Base (COD) system. Using the Match application, it was indicated that the hematite had been produced as the dominant phase. The existing of prepared hematite was revealed by the 2 theta crystal lattice at 33.1825 (237 a.u); 35.6613 (169 a.u); 49.5211 (101 a.u); 54.1099 (117 a.u); 62.4654 (72 a.u); and 64.0730 (86 a.u). The results also confirmed that the addition of sodium (NaOH) has no significant impact to hematite crystal. However, it can be seen clearly the sodium attached to the hematite surface, as shown in the results from XRD analysis.

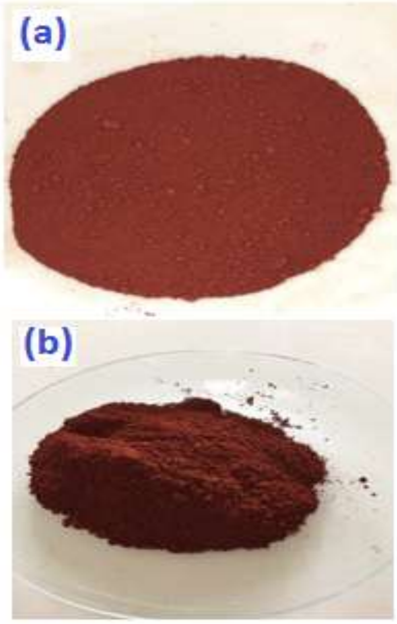

Figure 2; (a) the prepared hematit calcined at 700^{o}C for 2 h; (b) hematite particles impregnated with sodium

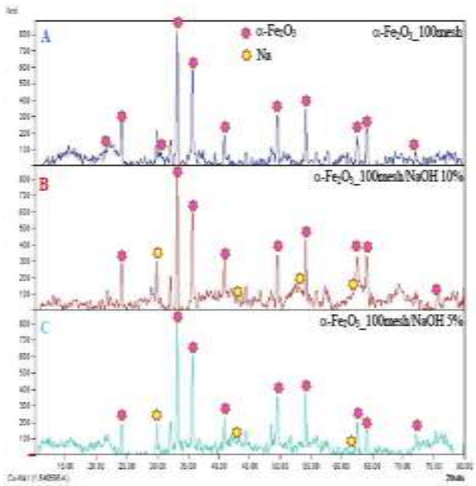

Figure 3 XRD pattern of; (a) the prepared hematite from Lhong iron mineral using precipation method with H_2SO_4; (b)the prepared hematite doped with NaOH of 5% (wt/wt); and (c) the prepared hematite doped with NaOH of 10% (wt/wt)

Another characterization using SEM-EDS showed that the morphology of the catalyst prepared from the iron mineral was more homogeneous while 5% NaOH added on the hematite material,as depicted in Fig. 3(b), compared to the hematite without any doping of NaOH, Fig. 3(a). However, in case of using higher concentration of NaOH (10% wt/wt) was used, the aglomeration taken place among the catalyst particles which reducing homogenity of the catalyst particles, as demonstrated in Fig. 3(c). Another chemical analysis, namely in order to find out the chemical composition of the prepared inorganic catalysts was conducted using Energy Dispersive X-Ray Spectroscopy (EDS).

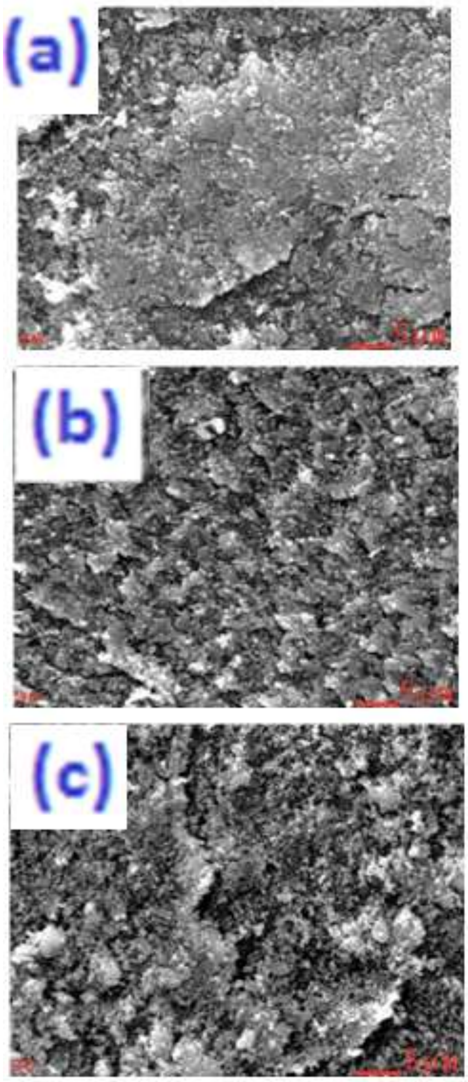

Figure 4. SEM images of; (a) the prepared hematite from Lhong iron mineral under precipation method with H_2SO_4;(b) the prepared hematite doped with NaOH of 5% (wt/wt); and (c) the prepared hematite doped with NaOH of 10% (wt/wt)

EDS data shown in Table 1 which could be noted that the amount of obtained hematite decreased slightly when sodium (Na) doped in the hematite which confirmed by decreasing the percentage of iron (Fe), as figured out in the table above.

Table 1 EDS data on the elemental composition of the prepared catalysts

Samples	Elemental Composition			
	O	**Fe**	**Al**	**Na**
Prepared hematite (α-Fe_2O_3)	27.92	69.66	2.42	-
Prepared hematite (α-Fe_2O_3) doped Na of 5% (wt/wt)	30.92	62.27	2.35	4.46
Prepared hematite (α-Fe_2O_3) of 10% (wt/wt)	30.07	62.60	2.35	4.78

Catalytic Activity on Transesterification of Coconut Oil

The biodiesel synthesis in this experiment was carried out using hematite doped with different amount of sodium metal (Na_2O/Fe_2O_3) as inorganic catalyst. Generally, it could be understood that the transesterification reactions at high temperatures can cause thermal oxidation reactions, namely the decomposition of chemical compounds contained in the oil. The thermal oxidation reaction taken place due to increasing the kinetic energy of the system, so that at the first step shows the reaction from the base of the catalyst with alcohol producing alkoxide and protonated catalyst. Then the alkoxide attacks the carbonyl group of triglycerides to form an intermediate compound alkyl ester and diglyceride anion. Furthermore, the protonated catalyst reacts with diglyceride anions to produce alkyl esters (biodiesel) and glycerol as by-products.

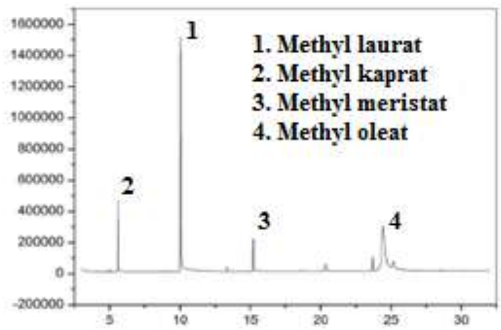

Figure 5. GC-Chromatogram of biodiesel products resulted from the transesterification reaction using hematite catalyst doped 5% (wt/wt) of NaOH (Na_2O/Fe_2O_3)

Based on the GC result exhibited in fig.5, it can be stated that the prepared catalyst shows catalytic activity on biodiesel synthesis, in spite of the synthesized biodiesel actually was produced with very small in quantity, only around 30.8%. Reffering to theoritical assumption, this can occur due to several factors including unreacted methanol and residual catalyst. The transesterification reaction requires one (1) mole of triglycerides to react with 3 moles of methanol to produce 1 mole of methyl ester fatty acid and 3 moles of glycerol. The optimal amount of methanol is needed so that the equilibrium shifts towards the reaction results, because the transesterification process is a reversible reaction.

Table 2 the alkyl compounds resulted throught transesterification reaction of coconut oil with methanol using different catalyst.

Inorganic catalyst	Biodiesel compounds
(α-Fe_2O_3	Methyl oleat, methyl pamitat,
α-Fe_2O_3doped Na of 5% (wt/wt)	Methyl oleat, methyl meristat, metyhyl laurat
α-Fe_2O_3 doped Na of 10% (wt/wt)	methyl oleat

Identification of synthesized biodiesel was done using GC-MS. Data on the main chromatogram peaks of alkyl ester are presented in Table 2. This study proved that the hematite modified with sodium was succesfully applied as on inorganic catalyst for transesterification reactions to produce biodiesel compound from coconut oil, eventhough the quality of the produced biodiesel is still relative lower from the SNI . The result of this experiment could be expected as a prospective scientific information in order to find an efficient inorganic catalyst for producingbiodieselwith its quality as well as the SNI standards.

CONCLUSION

The hematite (α-Fe_2O_3) was successfully prepared from local iron sand collected from Lhong region in Aceh Besar, Aceh by precipated with H_2SO_4. Furthermore, inorganic catalyst based on the hematite (α-Fe_2O_3) compound modified with sodium was successfully prepared in this study, whereas doping sodium (NaOH) on hematite mineral was enhanced the homogenity ofthe particle size with optimum concentration of NaOH was about 5% (wt/wt). Finally, the synthesized catalyst (Na_2O/Fe_2O_3) showed its catalytic activity on transterification reaction of coconut oil with methanol for producing alkyl ester as the biodiesel compound.

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